J Appl Electrochem (2014) 44:345–352
DOI 10.1007/s10800-014-0661-7

RESEARCH ARTICLE

Electron-beam-irradiated polyethylene membrane with improved electrochemical and thermal properties for lithium-ion batteries

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Received: 22 September 2013 / Accepted: 2 January 2014 / Published online: 11 January 2014

Abstract The effects of electron-beam irradiation on the physicochemical and electrochemical properties of polyethylene (PE) separators are investigated. The high-energy electron-beam irradiation creates carbonyl bands on the surface of bare PE separators, however, it does not affect morphology and pore structure of the separators. In addition, cells employing the electron-beam-irradiated PE separators clearly exhibit better ionic conductivity and rate capability without any degradation in cycling performance compared to cells employing the bare PE separator. This improvement is explained by a formation of new functional group on PE surface—the electron-beam irradiation creates carbonyl group on the surface of the PE separator and it readily facilitates the migration of Li^+ and improves solvent affinity of the PE separators. Furthermore, the thermal stability of PE separators is effectively enhanced by irradiating them with electron beams. The thermal shrinkage of the electron-beam-irradiated PE separators is observed to be much lower than that of bare PE separators, resulting in an increased gap between the shut-down and melting integrity temperatures. From these results, it is believed that the electron-beam irradiation can be considered as an effective approach to enhance electrochemical and thermal properties of PE separator.

Keywords Electron-beam irradiation · PE separator · Lithium-ion battery · Thermal and electrochemical properties

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1 Introduction

Lithium-ion batteries have been widely considered a potential power source because of their high energy and power density. However, they may pose safety risks because they are composed of high-energy materials and flammable electrolytes such as cyclic or linear carbonates. Separators are regarded as critical components that insure the safe use of lithium-ion batteries because their main function is to prevent electrical short circuits between the positive and negative electrodes [1, 2]. Although polyethylene (PE) separators are currently being used in lithium-ion batteries because of their good electrochemical stability and mechanical strength, there are safety concerns associated with the use of lithium-ion batteries at temperatures higher than 140 °C due to the poor thermal properties of these separators [3–5]. Consequently, overcoming this drawback of PE separators remains the greatest challenge.

Many efforts such as the use of ceramic-coated separators and non-woven separators have been made to solve this shortcoming of PE separators. Ceramic-coated separators are composed of ceramic particles and a polymeric binder coating on the PE separator. Several studies reported that ceramic-coated separators exhibit better thermal properties than practical PE separators because ceramic particles act as heat-resistant materials [6–8]. However, ceramic-based separators are likely more expensive because they consist of additional ceramic particles and polymeric binder. Non-woven separators have been intensively studied for use in lithium-ion batteries with the goal of achieving superior thermal properties [9, 10]. Despite the good thermal stability of such separators, their practical use in lithium-ion batteries is limited owing to their poor mechanical properties compared with those of PE separators. In addition, it is difficult to control the pore size and thickness as well as the uniformity

of the pore distribution. It is therefore necessary to improve the thermal properties of PE separators without causing considerable cost increase or performance trade-off.

It is well-known that gamma-ray and electron-beam irradiation can be effectively used to modify the physicochemical properties and to improve the thermal properties of PE [11–14]. Our group has also reported the positive effects of gamma-ray irradiation on the thermal and physicochemical properties of PE separators [15]. Gamma-ray irradiation is widely used to modify the surface and structural properties of polymers because of its higher penetration ability. However, it is difficult to directly incorporate gamma-ray irradiation in the assembly line of lithium-ion batteries because of a long processing time and high equipment cost. Electron-beam irradiation is another powerful method for overcoming these drawbacks of gamma-ray irradiation. It has many advantages such as short process time, in-line process, low equipment cost, and short release time [16–18]. Consequently, electron-beam irradiation is much more attractive than gamma-ray irradiation in terms of processing cost, processing time, and availability for modifying the physicochemical properties and improving the thermal properties of PE.

With these considerations in mind, PE separators were prepared by electron-beam irradiation. Here, the following aspects are discussed: (i) method for changing the thermal properties of PE separators using electron-beam irradiation and (ii) the effect of electron-beam irradiation on the physicochemical and electrochemical properties of PE separators.

2 Experimental

Bare PE separators (Asahi Korea Chemicals) were irradiated by an electron beam in an air atmosphere at room temperature to modify their physicochemical properties. The applied radiation dose was 100, 150, and 200 kGy. To characterize the surface functionalities of the PE separators after electron-beam irradiation, bare and electron-beam-irradiated separators were analyzed using a Fourier-transform infrared spectrometer (FT-IR; Bomem MB100 Spectrometer), with the wavenumber ranging from 400 to 4,000 cm^{-1} (resolution 4 cm^{-1}), operated in the absorption mode under N_2 atmosphere in a dry room in which the dew point was below −60 °C. The morphological changes were analyzed using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7000F). A Gurley-type densometer (Toyoseiki) was used to measure the air permeability of the bare and electron-beam-irradiated separator. The ionic conductivity was obtained from the relation $\sigma = d/RA$, where d and A are the thickness and area of the separators, respectively, and R is the electrolyte resistance measured by an AC impedance test at room temperature. The AC impedance was measured using a Solartron 1280C over a frequency range of 0.1–20,000 Hz with an AC amplitude of 10 mV. A 2032 coin-type cell was assembled by sandwiching the prepared separators between two Li-metal electrodes and then soaking it in a liquid electrolyte for AC impedance measurements. The thermal shrinkage of the prepared separators was determined by measuring the dimensional changes of the bare and electron-beam-irradiated separators after storage at 120 °C for 1 h. Samples with dimensions of 5 cm (width) × 5 cm (length) were prepared and kept in a 120 °C oven for 1 h. The changes in the separators' dimensions were then calculated using Eq. (1):

$$\text{Shrinkage } (\%) = \frac{W_i - W_f}{W_i} \times 100, \quad (1)$$

where W_i is the initial area and W_f is the final area of the separator after the storage test.

The shut-down properties of the separators were obtained by measuring their impedance at 1 kHz using a Hioki 3560C AC Hitester. A coin-type cell, consisting of $LiCoO_2$ as the positive electrode and graphite as the negative electrode, was connected to the impedance tester and placed in a temperature-controlled oven at room temperature. The temperature was then increased at a rate of 2 °C min^{-1}, and the impedance was recorded every 10 s.

The electrochemical performance of the prepared separators was examined using 2032 coin-type full-cells, which were composed of the prepared separators, a cathode [$LiCoO_2$ (active material):polyvinylidene fluoride (PVdF, binder):Super-P (conducting agent) = 95:3:2 wt%, capacity per unit area = 3.8 ± 1 mAh cm^{-2}], and an anode [graphite (active material):carboxymethylcellulose (CMC, viscosity agent):styrene–butadiene rubber (SBR, binder) = 97.5:1:1.5 wt%, capacity per unit area = 4.1 ± 1 mAh cm^{-2}]. The liquid electrolyte was composed of 1 M $LiPF_6$ in ethylene carbonate/ethyl methyl carbonate (3:7 by volume, PANAXETEC) and 3 wt% vinylene carbonate additive. The rate discharge tests were performed in the voltage range of 3.0–4.2 V at currents of 0.2, 0.5, 1.0, 2.0, and 3.0 C. The cycling performance was examined in constant-current mode at 0.5 C from 3.0 to 4.2 V using a cycle tester (Maccor 8500). All electrochemical tests were conducted at room temperature.

3 Results and discussion

3.1 Physicochemical and electrochemical performance of the electron-beam-irradiated PE separators

The prepared PE separators were irradiated by various doses of electron-beam irradiation to determine the effects of electron-beam irradiation on their physicochemical and

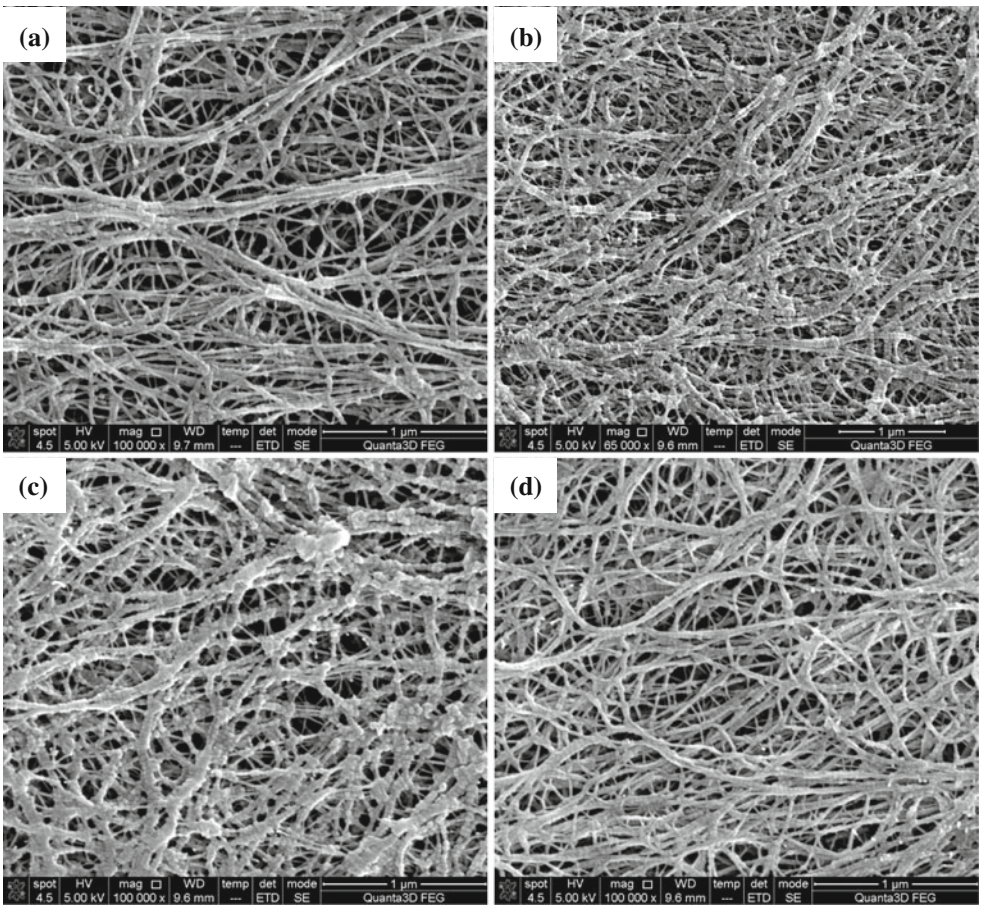

Fig. 1 Microstructure of **a** bare PE separator, **b** 100 kGy electron-beam-irradiated PE separator, **c** 150 kGy electron-beam-irradiated PE separator, and **d** 200 kGy electron-beam-irradiated PE separator

electrochemical properties. The microstructures of the bare and electron-beam-irradiated PE separators were analyzed using FE-SEM, as shown in Fig. 1. The results did not reveal any visible differences between the microstructures of the bare and electron-beam-irradiated PE separators. In addition, the air permeability of these separators was measured to clarify the change in their inner pore structure. The PE separators irradiated by 100-, 150-, and 200-kGy electron beams exhibited values of 233, 232, and 236 s 100 cc^{-1}, respectively, which are similar to the Gurley number of bare PE separators (238 s 100 cc^{-1}). These observations confirmed that the microstructures and pore structures of the PE separators were not influenced by electron-beam irradiation.

To clarify the effects of electron-beam irradiation on the PE separators, the rate capabilities of 2032 coin-type full-cells employing separators prepared by irradiation were measured for various doses of electron-beam irradiation at current densities of 0.2, 0.5, 1.0, 2.0, and 3.0 C. As shown in Fig. 2, the bare and 100-kGy electron-beam-irradiated PE separators exhibited similar capacity retentions of 31.0

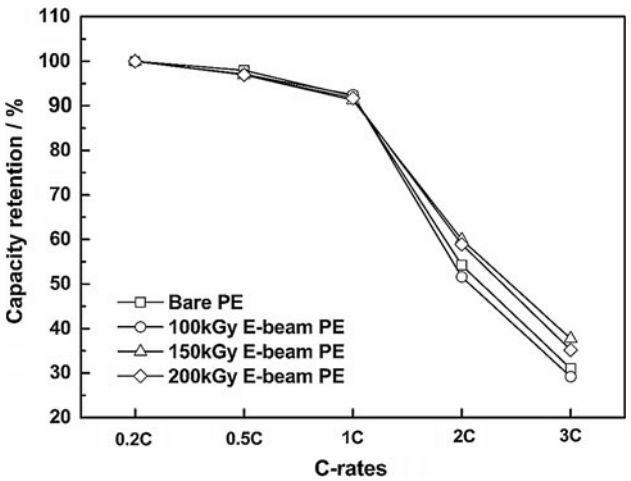

Fig. 2 Rate capabilities at current of 0.2, 0.5, 1.0, 2.0, and 3.0 C depending on separators. The cells were tested in the voltage range of 3.0–4.2 V at room temperature (*square* bare PE, *circle* 100 kGy E-beam PE, *triangle* 150 kGy E-beam PE, and *diamond* 200 kGy E-beam PE)

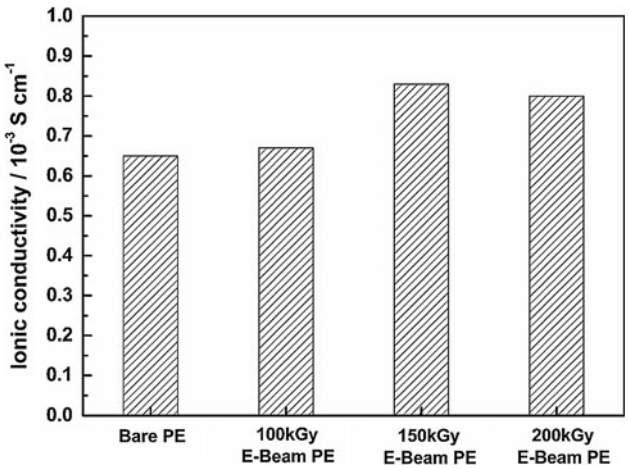

Fig. 3 The results for ionic conductivities of bare and electron-beam-irradiated PE separators

and 29.2 %, respectively, at a high current density of 3.0 C, whereas the 150- and 200-kGy electron-beam-irradiated PE separators exhibited much higher capacity retentions of 37.8 and 35.2 %, respectively, at the same current density. To investigate the reason behind this improvement in the rate discharge properties with increasing electron-beam irradiation dose, the ionic conductivity was measured because of the strong correlation between the rate capability and ionic conductivity. Figure 3 shows the ionic conductivity of the bare and electron-beam-irradiated PE separators. The ionic conductivity of the 100-kGy electron-beam-irradiated separator (6.7×10^{-4} S cm^{-1}) is clearly almost the same as that of the bare PE separator (6.5×10^{-4} S cm^{-1}), whereas the 150- and 200-kGy electron-beam-irradiated separators exhibit higher ionic conductivities of 8.3×10^{-4} and 8.0×10^{-4} S cm^{-1}, respectively. This result is well-suited for explaining the improvement in the rate capability. In general, the ionic conductivity and rate capability are strongly influenced by the ion transport pathways related to the air permeability of the PE separators. Interestingly, the ionic conductivity and rate capability were found to be affected by the electron-beam irradiation dose even though the microstructures and air permeability of the electron-beam-irradiated PE separators were similar to those of the bare PE separator. These results imply that molecular structural changes or other reactions may occur in the PE separator following electron-beam irradiation, while the microstructures of the PE separator are maintained. To verify this hypothesis, the bare and electron-beam-irradiated PE separators were analyzed using FT-IR. As shown in Fig. 4a, the typical characteristic bands associated with the PE separator appear at 2,850–3,000 cm^{-1} (C–H stretching vibrations) and 1,465 cm^{-1} (C–H bending vibration) regardless of the electron-beam irradiation. However, as shown in Fig. 4b, following electron-beam irradiation, there is a visible

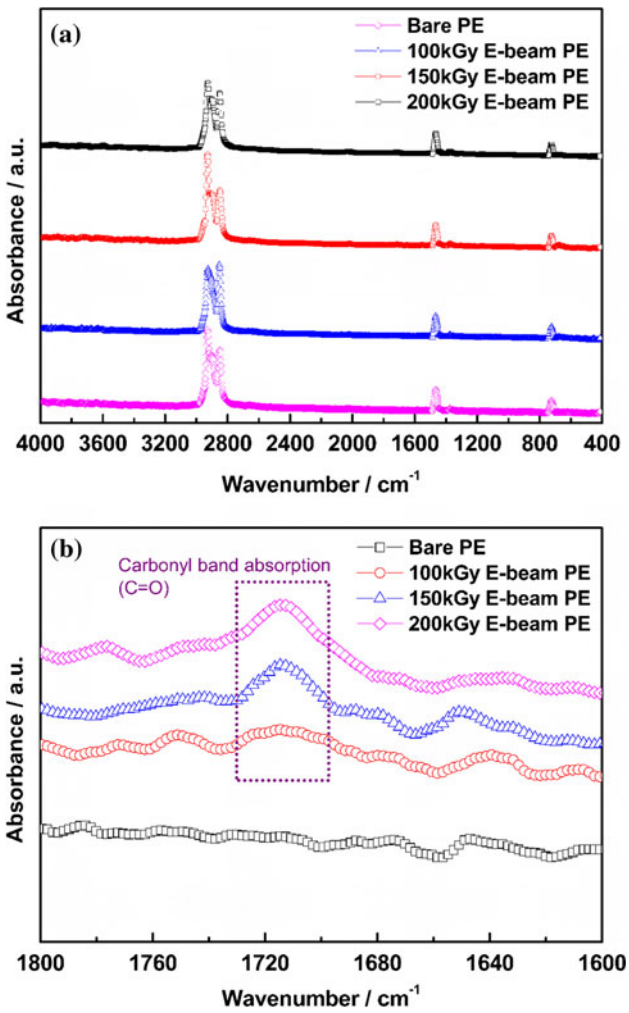

Fig. 4 FT-IR spectra of bare and electron-beam-irradiated PE separators: **a** range of 400–4,000 cm^{-1} and **b** range of 1,600–1,800 cm^{-1}

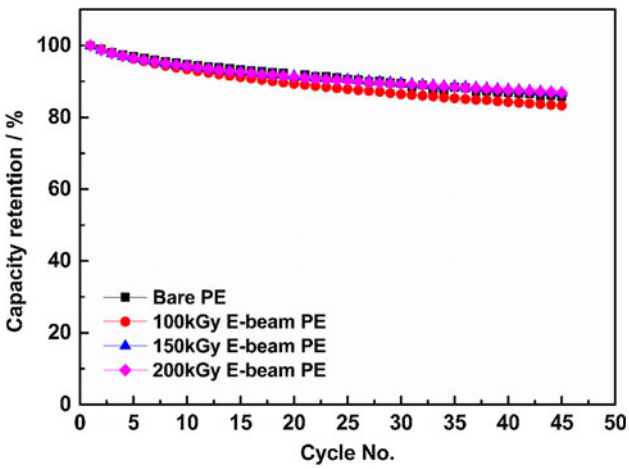

Fig. 5 Cyclic performance of bare and electron-beam-irradiated PE separators. The cells were tested in the voltage range of 3.0–4.2 V at room temperature in a constant-current mode at 0.5 C (*black* bare PE, *red* 100 kGy E-beam PE, *blue* 150 kGy E-beam PE, and *pink* 200 kGy E-beam PE)

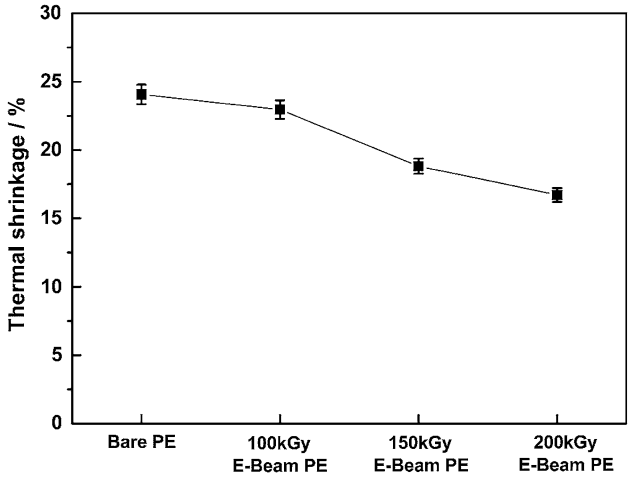

Fig. 6 Degree of thermal shrinkage of bare and electron-beam-irradiated PE separators after storage at 120 °C for 1 h

difference at around 1,720 cm^{-1}, which corresponds to the carbonyl band. The carbonyl band is not observed for the bare and 100-kGy electron-beam-irradiated PE separators, whereas it is clearly observed for the 150- and 200-kGy electron-beam-irradiated PE separators. This result indicates that the molecular structure of the PE separator changes because of high-energy electron-beam irradiation. Although a compelling explanation for the changes in a PE separator is yet to be presented, many researchers have assumed that chemical changes in polymers might occur in the following sequence: (i) scission of polymeric chains (breakage of C–H bonds) by electron-beam irradiation, which is one of the high-energy sources; (ii) formation of reactive radical species on carbon; (iii) termination by C–C bond formation, resulting in the generation of highly crosslinked PE. Because this reaction is accompanied by the formation of carbonyl groups as a result of a reaction with oxygen in the air, the observance of a carbonyl signal in an FT-IR spectrum is considered an indicator of further crosslinking reaction of PE [13, 16–22]. In addition, the polar solvent affinity of the PE separators is improved by the carbonyl bands [20]. These observations indicate that the molecular structural changes such as the creation of carbonyl bands induced by high-energy electron-beam irradiation additionally facilitate Li^+ migration and improve the polar solvent affinity of the PE separators,

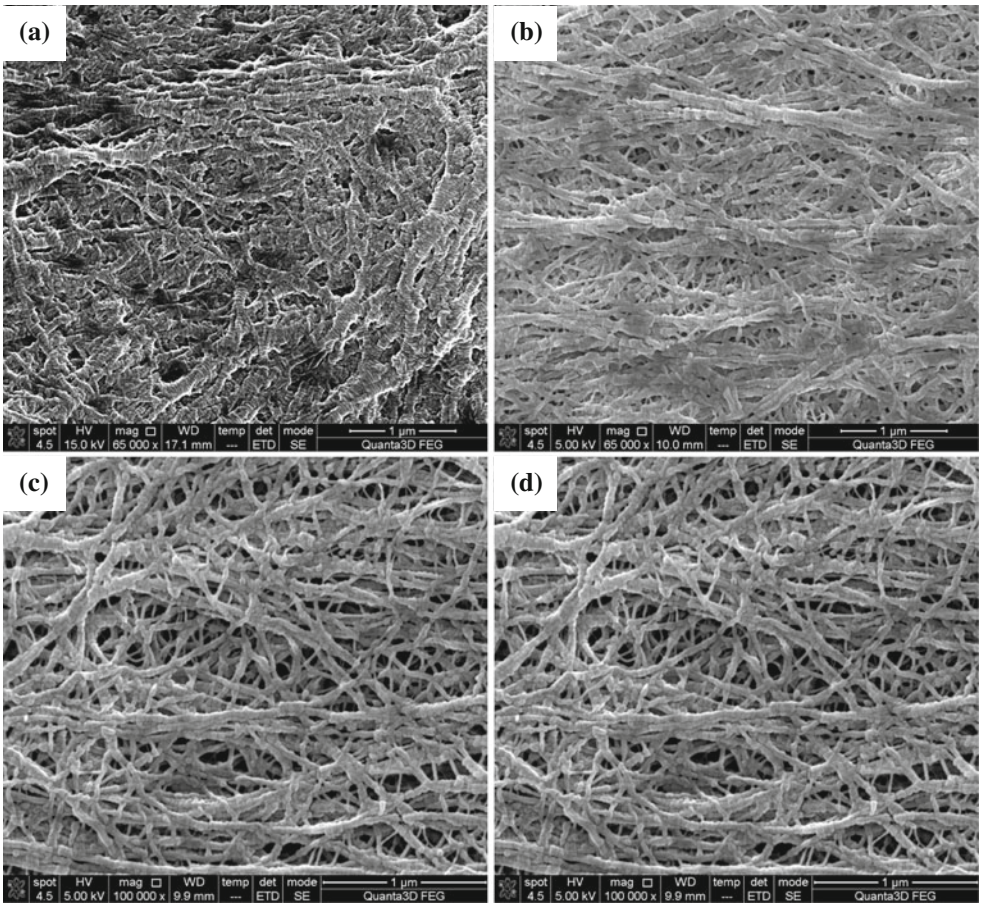

Fig. 7 Microstructures of PE separators after storage at 120 °C for 1 h: **a** bare PE separator, **b** 100 kGy electron-beam-irradiated PE separator, **c** 150 kGy electron-beam-irradiated PE separator, and **d** 200 kGy electron-beam-irradiated PE separator

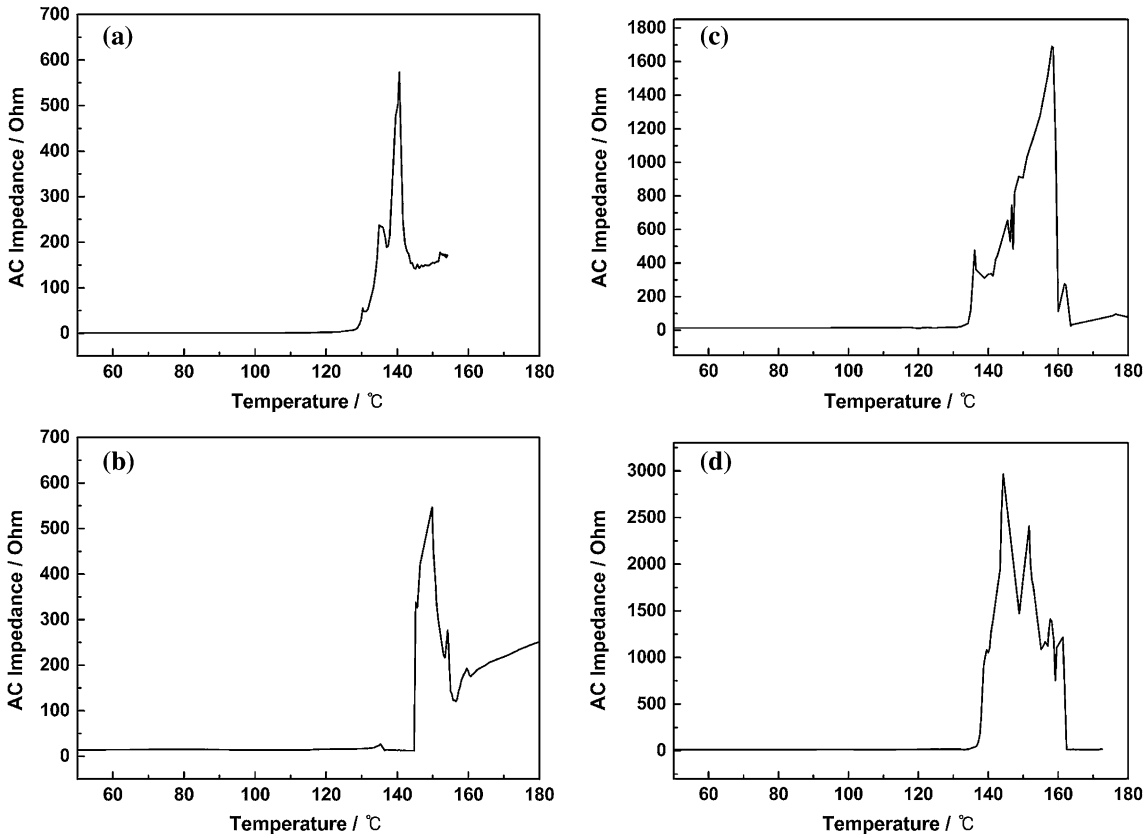

Fig. 8 Results for shut-down properties depending on separators. AC impedance was measured at 1 kHz with increasing temperature (2 °C min^{-1}): **a** bare PE separator [15], **b** 100 kGy electron-beam-irradiated PE separator, **c** 150 kGy electron-beam-irradiated PE separator, and **d** 200 kGy electron-beam-irradiated PE separator

leading to a better ionic conductivity and rate capability. Figure 5 shows the cycling performance results for cells assembled with PE separators prepared by irradiation with various electron-beam doses. There is not much difference between the cycle life of cells having electron-beam-irradiated PE separators and cells having bare PE separators. This reveals that the electron-beam irradiation does not have any negative effects on the cycling performance of lithium-ion batteries.

3.2 Thermal properties of electron-beam-irradiated PE separators

To evaluate the thermal stability of the electron-beam-irradiated PE separators, the separators that were prepared using various electron-beam irradiation doses were stored at high temperature (120 °C) for 1 h. Subsequently, the thermal shrinkage of these separators was measured, and these results are plotted in Fig. 6. The bare PE separator exhibited a thermal shrinkage of 24.1 %, whereas the 100-kGy electron-beam-irradiated PE separators exhibited a slightly lower thermal shrinkage (23.0 %). The thermal shrinkages of the 150- and 200-kGy electron-beam-irradiated PE separators were 18.8 and 16.7 %, respectively. In other words, the thermal shrinkage gradually improved with increasing electron-beam irradiation dose. After the separators were stored at 120 °C for 1 h, visible changes were observed in their surface morphologies, as shown in Fig. 7. The porous microstructure of the bare PE separator collapsed, whereas the 150- and 200-kGy electron-beam-irradiated PE separators maintained their porous microstructures. It has generally been reported that the thermal properties of PE separators are dramatically improved by cross-linking as they are exposed to a high-energy irradiation [15, 21]. Therefore, this improvement in the thermal stability might be explained by the cross-linking of the PE separators by electron-beam irradiation.

It is well-known that a separator with good thermal resistance generally exhibits a large gap between the shut-down and melting integrity temperatures [2]. Therefore, to further understand the effects of electron-beam irradiation on the thermal properties of a PE separator, a shut-down test was performed; the results are shown in Fig. 8. It appears that the bare PE separator exhibits a narrower gap between the shut-down and melting integrity temperatures than the 150- and 200-kGy electron-beam-irradiated PE separators. In addition, the gap between these temperatures dramatically increased when the bare PE separator was

irradiated by a higher electron-beam irradiation dose. It is likely that many more polymer chains on the PE separator may become actively cross-linked by higher energy irradiation. This is consistent with the thermal shrinkage results described above. These observations suggest that safety issues such as a hot box, overcharge, and nail penetration can be satisfactorily improved by employing the electron-beam-irradiated separators in lithium-ion batteries because of the improvement in the thermal resistance of the bare PE separator due to electron-beam irradiation. According to the results, it is confirmed that the electron-beam irradiation is an effective approach to enhance electrochemical and thermal properties in terms of efficiency and processability.

4 Conclusions

This study proposes that electron-beam irradiation is effective in enhancement of properties of PE separator without degradation of their physiochemical or electrochemical properties. The electron-beam irradiation enables installation of carbonyl group on the bare PE separator, it leads to facilitating Li^+ migration and improving the solvent affinity of the PE separator, resulting in better ionic conductivity and rate discharge capability. In addition, the thermal stability is remarkably enhanced—the electron-beam-irradiated PE separators exhibit a lower thermal shrinkage ratio at 120 °C compared to the bare PE separator. The differences between the shut-down and melting integrity temperatures of the bare and electron-beam-irradiated PE separators are observed—the gap between these temperatures is found to dramatically increase because of the cross-linking of the PE separator by electron-beam irradiation. Therefore, the safety concerns regarding lithium-ion batteries such as a hot box, overcharge, and nail penetration could be satisfactorily addressed by employing electron-beam-irradiated separators owing to the improvement in the thermal resistance.

Acknowledgments This work was supported by the Energy Efficiency and Resources program of the Korea Institute of Energy Technology Evaluation and Planning (Project No. 20112010100140) and R&D program (Project No. 10041942) of the Ministry of Trade, Industry, and Energy, Republic of Korea.

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